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KINETICS OF THE REACTION BETWEEN HYDROXYLAMINE AND SODIUM BISULFITE

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ABSTRACT

Hydroxylamine and sulfur dioxide react in aqueous solution to form either sulfamic acid or ammonium bisulfate. Rate studies have been performed as a function of temperature. The rate law has been determined. The enthalpy and entropy of activation for the formation of both sulfamic acid and ammonium bisulfate have been evaluated.

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I. Introduction

Sisler and Audrieth¹ studied the formation of sulfamic acid by the reaction of hydroxylamine with sulfur dioxide in an aqueous solution and proposed that the reaction mechanism involved coordination between NH_2OH and SO_2 molecules with subsequent rearrangement to sulfamic acid. The kinetics of this reaction was investigated by Brackman and Higginson² at room temperature. They found that in addition to sulfamic acid, trace amounts of ammonium bisulfate were also formed and that the percentage of ammonium bisulfate produced appeared to be independent of pH. Fraser³ studied the kinetics of this reaction as a function of temperature. The kinetic studies by both Brackman and Higginson² and Fraser³ were performed by monitoring the rate of disappearance of total sulfite during the course of the reaction. This paper reports a kinetics study of the reaction by monitoring the concentration of total hydroxylamine.

Because hydroxylamine is one of the species produced⁶⁻⁸ as a result of interaction between SO_2 and NO_x in aqueous solution, a thorough characterization of the kinetics of reactions between hydroxylamine and bisulfite is essential to understand the importance of SO_2 and NO_x interaction in atmospheric aqueous droplets in terms of acid rain formation,⁷ and to develop a flue gas wet simultaneous desulfurization and denitridication process.⁸

II. Experimental

Apparatus. A PAR Model 174 polarograph was used to determine the concentration of hydroxylamine. A dropping mercury electrode was used as the working electrode, and platinum wire and a saturated calomel electrode (SCE) with a LiCl salt bridge were used as counter and reference electrodes respectively. pH measurements were made with a Corning Model 135 pH meter. Temperature was controlled with a Polyscience Model 90T thermostat.

Chemicals. All chemicals were of reagent purity. The 0.1 M hydroxylamine standard solution was prepared from $\text{NH}_2\text{OH}\cdot\text{H}_2\text{SO}_4$. The sodium bisulfite solution was prepared from $\text{Na}_2\text{S}_2\text{O}_5$ daily. Robinson and Stokes pH 5 buffer was prepared from 0.5 M Na_2HPO_4 and 0.5 M NaOH solutions.

Procedure. The reaction mixture was prepared by aliquoting to a 100-ml volumetric flask in the following sequence — hydroxylamine stock solution, buffer solution, and finally sodium bisulfite. The flask was quickly made to volume with the distilled water after the last addition and mixed; then the first polarographic determination of the hydroxylamine concentration was made. Subsequent measurements were made after the appropriate time intervals to monitor the time rate of disappearance of hydroxylamine. For some of the work the solutions were thermostatted.

For the polarographic determination 10.0 ml of the reaction mixture was transferred into a 100-ml measuring flask, 2.0 ml of 1 M LiCl solution (and 4 ml of buffer solution of pH 5 if necessary) was added; and the polarograph curve in the potential range from -1.0 V and -1.7 V vs. SCE was recorded in the differential pulse polarographic mode. Instrumental conditions were: amplitude, 25 mV; scan rate, 5 mV s^{-1} ; drop time, 2 sec. The concentrations were calculated on the basis of standard addition method or calibration curves.

Results. The first set of experiments determined the reaction order with respect to total hydroxylamine. An excess of bisulfite was used, and the solution was buffered at pH 5 in these runs. Figure 1 shows a semi-log plot of total hydroxylamine concentration vs. time for several initial concentrations. Parallel lines indicate a first order dependence on hydroxylamine.

The dependence of the reaction on total sulfite was determined by varying the excess sulfite concentration for a fixed hydroxylamine concentration at

pH 5. Because the hydroxylamine is first order as determined above, one can write the rate law as

$$-\frac{d[\text{total hydroxylamine}]}{dt} = k_{\text{obs}} [\text{total hydroxylamine}] [\text{total sulfite}]^n,$$

where one can define

$$Q = -\frac{d \ln[\text{total hydroxylamine}]}{dt} = k_{\text{obs}} [\text{total sulfite}]^n.$$

A log-log plot of Q vs. $[\text{total sulfite}]$ should give a straight line with the slope equal to the order of the reaction with respect to total sulfite. Fig. 2 shows the the slope is 0.94, which is regarded as first order dependence. Therefore, the reaction follows the rate law

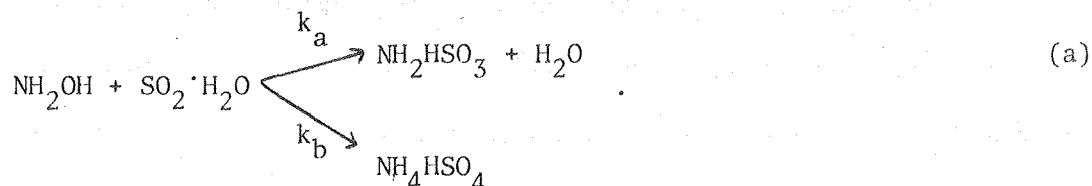
$$-\frac{d[\text{total hydroxylamine}]}{dt} = k_{\text{obs}} [\text{total hydroxylamine}] [\text{total sulfite}]. \quad (1)$$

The rate constant k_{obs} in 1/mole-sec was determined at two temperatures: 7.67×10^{-3} at 35°C and 1.48×10^{-3} at 22°C . The rate of reaction was found to be independent of the ionic strength of the solution.

III. Calculation and Discussion

Hydroxylamine and sulfur dioxide react in aqueous solution to form sulfamic acid and traces of ammonium bisulfate. Brackman and Higginson² found that the rate of formation of sulfamic acid and of ammonium bisulfate have the same dependence on pH and reactant concentrations. They thus concluded that both products involve the same transition complex. These authors ruled out the reaction mechanism involving HSO_3^- and NH_2OH species. Sisler and Audrieth¹

and Fraser³ suggested that formation of both sulfamic acid and ammonium bisulfate involves attack by the $\text{SO}_2 \cdot \text{H}_2\text{O}$ on the NH_2OH . The reaction can therefore be expressed as



The rate law can be written as

$$-\frac{d[\text{total hydroxylamine}]}{dt} = (k_a + k_b) [\text{NH}_2\text{OH}] [\text{SO}_2 \cdot \text{H}_2\text{O}] \quad (2)$$

To evaluate the rate constant and activation energy of both reactions using our experimental measurements, Eq. (1) is expressed in terms of the concentration of reaction species NH_2OH and $\text{SO}_2 \cdot \text{H}_2\text{O}$. Because $[\text{total hydroxylamine}] = [\text{NH}_2\text{OH}] + [\text{NH}_3\text{OH}^+]$ and $[\text{total sulfite}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{=}]$, Eq. (1) can be rewritten as

$$-\frac{d[\text{total hydroxylamine}]}{dt} = k_{\text{obs}} \left(1 + \frac{[\text{H}^+]}{K_n}\right) \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}\right) [\text{NH}_2\text{OH}] [\text{SO}_2 \cdot \text{H}_2\text{O}] , \quad (3)$$

where K_n , K_1 , and K_2 are respectively the acid dissociation constant for hydroxylamine³ and the first and second dissociation constants for sulfurous acid.⁴

By comparing Eqs. (2) and (3), we obtain the following relationship:

$$k_a + k_b = k_{\text{obs}} \left(1 + \frac{[\text{H}^+]}{K_n}\right) \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}\right) .$$

The ratio k_a/k_b can be obtained by the corresponding ratio of the products $[\text{NH}_2\text{HSO}_3]/[\text{NH}_4\text{HSO}_4]$; this ratio was determined by Brackman and Higginson² and Fraser³ at several temperatures. The following values, obtained from the interpolation of Fraser's result were used: 9 at 22°C and 19 at 35°C. By applying the transition-state theory,⁵ the enthalpy and entropy of activation for the formation of both sulfamic acid and ammonium bisulfate can be calculated as shown in Table 1. The results of this study are in fairly good agreement with those of Fraser.

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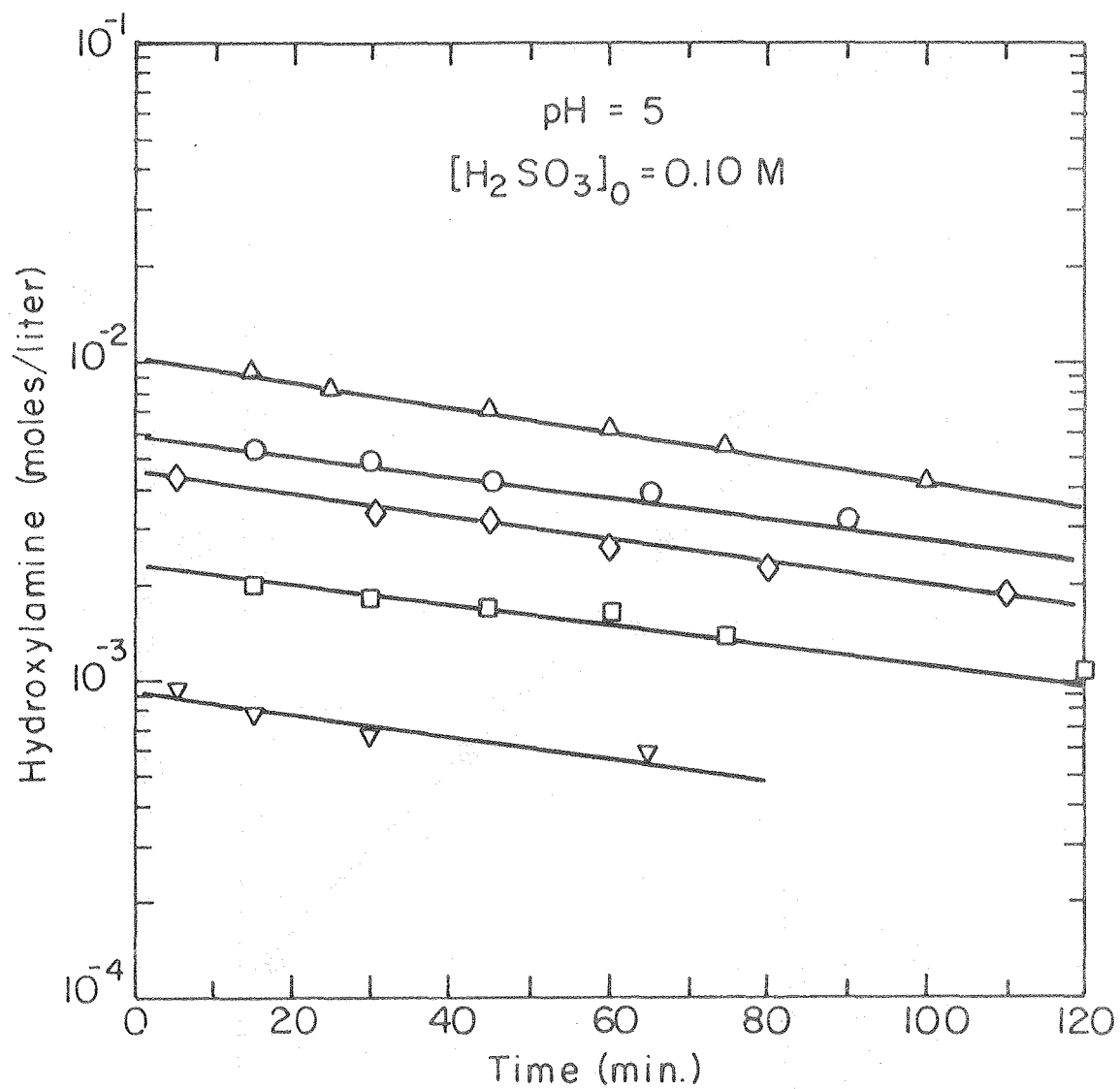
Table 1. The enthalpy and entropy of activation for the formation of sulfamic acid and ammonium bisulfate by the reaction of NH_2OH with $\text{SO}_2 \cdot \text{H}_2\text{O}$.

	Sulfamic acid		Ammonium bisulfate	
	ΔH_a^\ddagger (kcal/mole)	ΔS_a^\ddagger (e.u.)	ΔH_b^\ddagger (kcal/mole)	ΔS_b^\ddagger (e.u.)
Fraser	10.9	-16	1	-56
This work	13.4	- 6.1	3.0	-45.8

Figure Captions

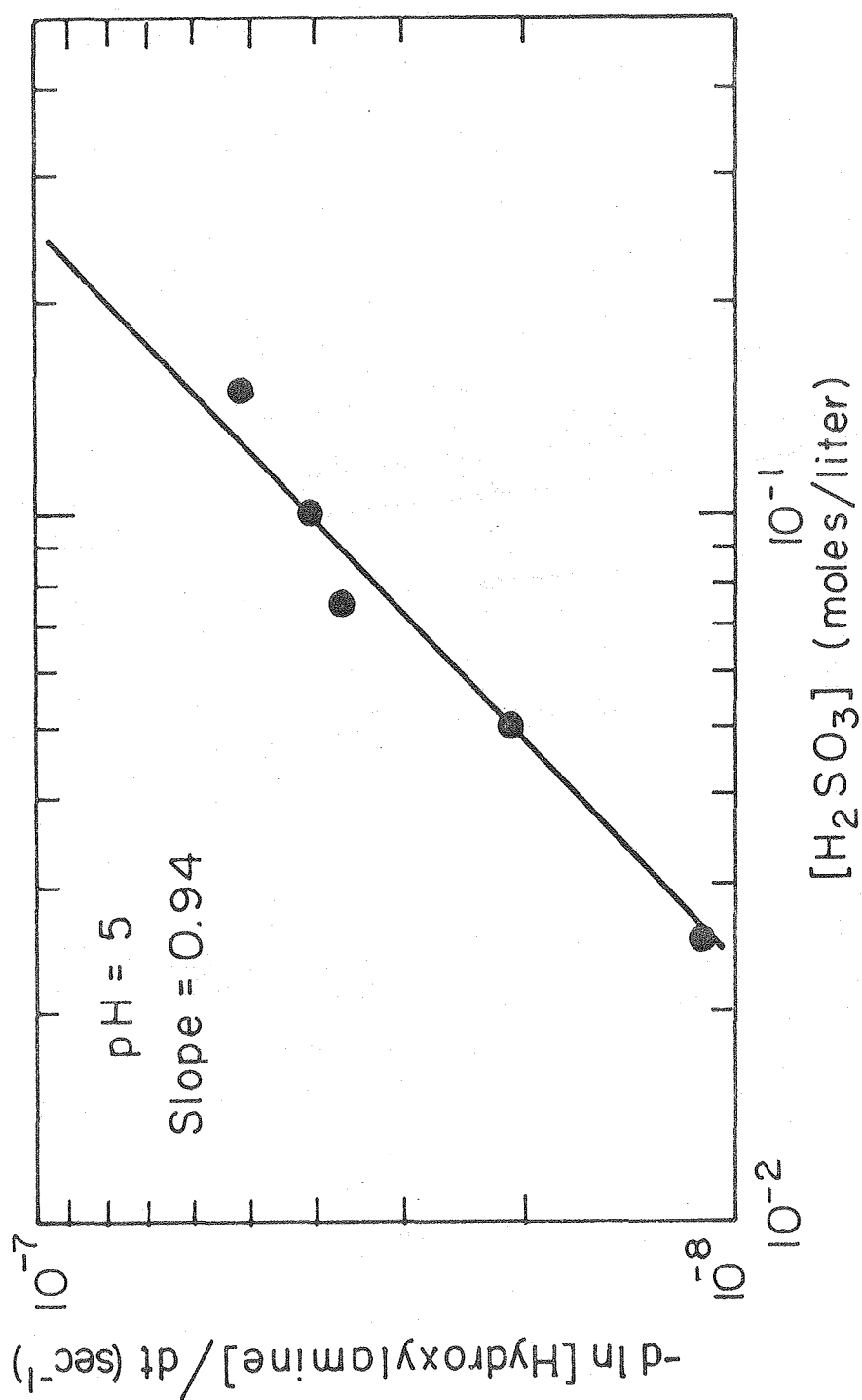
Figure 1. Loss of hydroxylamine as a function of time. Straight lines indicate first order dependence. $[\text{H}_2\text{SO}_3]$ indicates total sulfite, S(IV) concentration.

Figure 2. Dependence of the rate on total sulfite concentration. The slope is the order of the reaction with respect to sulfite.



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Figure 1



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Figure 2